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Potential impact of CO_2 storage on subsurface microbial ecosystems and implications for groundwater quality

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Abstract

The success of carbon capture and storage (CCS) projects depends on the ability of storage sites to contain CO_2 without leakage; and the ability to convince regulators and the general public in the safety of the technology. If leakage were to occur after formal closure of the injection site, this could be over small areas from discrete point sources, such as abandoned wells, resulting in localised high concentrations of CO_2 in near-surface ecosystems. Consequently, studies of the potential environmental consequences of CCS have focused on near-surface ecosystems and, as a result, environmental impacts of localised elevated CO_2 on terrestrial and marine ecosystems are areas of active research. However, a CO_2 storage site, in itself, could also impact on deep subsurface microbial ecosystem and biogeochemical processes, potentially affecting groundwater quality. Using a microbial energetics approach, the significance of these impacts can be scoped with a simple evaluation tool.

Keywords: Microbial ecosystems; impacts; CO_2 storage; groundwater; modelling

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1. Introduction

The success of carbon capture and storage (CCS) projects depends on the ability of storage sites to contain CO_2 thus mitigating releases to the atmosphere. However, concerns about the technology have been raised in many countries and have resulted in difficulties in implementing projects (e.g. Netherlands). These concerns usually focus on the effects of possible leakages from storage sites and the potential large-scale environmental consequences of CCS. To date, studies have focused on the physical and chemical isolation of CO_2 in stable geological formations, with associated monitoring systems to assure that no significant leakage occurs to the surface. If leakage was to occur after formal closure of the injection site, this could be over small areas from discrete point sources, such as abandoned wells, resulting in locally high concentrations of CO_2 in near-surface ecosystems. Consequently, environmental impacts of localised elevated CO_2 on terrestrial and marine ecosystems are areas of active research [e.g. 1,2,3]. However a CO_2 storage site could also directly impact deep subsurface microbial ecosystems and biogeochemical processes.

An observation based on other industrial activities that can perturb the deep geosphere is that microbiological effects develop only slowly. The initial perturbation often changes the conditions to which indigenous populations have adapted, resulting in a decrease in their activity levels. If the perturbation is not radical enough to sterilise the surroundings, however, new communities may evolve over periods of years or decades. More critically, if the activity introduces nutrients into a hyper-oligotrophic (low nutrient) system, the activity of the new population may be very much higher than that originally present, leading to major environmental changes as illustrated in acid mine drainage (e.g. Evangelou and Zhang [4] as an overview to the vast literature of biogenic acid mine drainage). There is certainly potential for CO_2 injection to cause such a perturbation – at least in some geological settings – although the scale and likely significance has yet to be established. Given both the huge costs of remediation and the potential for bad publicity that could damage CCS implementation plans globally, the precautionary principle suggests that this factor should be carefully assessed before a storage project is initiated.

2. Subsurface microbiological ecosystems and CO_2 storage

It is well recognised that microbes live in a wide range of subsurface environments, even if growth is strongly constrained by limited nutrient and energy supplies resulting in very low metabolic rates [5,6,7,8]. Indeed, it has been estimated that the mass of subsurface microbes may exceed the mass of biota on the Earth's surface [9]. Thus it is almost certain that microbes can be found in the geological settings considered for CO_2 storage and, consequently, they could be affected by injected CO_2. Whilst it is extremely unlikely that microbes could survive exposure to supercritical CO_2 because of its physical and chemical properties [10], many will survive, and may thrive, in contact with the gaseous or dissolved CO_2 phases [11].

An indirect effect of CO_2 results from the alteration of groundwater pH which, in turn, will influence the size and makeup of microbial populations. A more direct effect is the potential role of CO_2 as an oxidant that can be utilised as an energy source by a range of different methanogenic organisms in strongly reducing environments [12]. Consequently, it is important to examine the consequences of microbially catalysed methanogesis, either in terms of behaviour of resultant methane or associated oxidation of reactive minerals, such as sulphides. The latter process could lead to the mobilisation of trace metals, as has been proposed elsewhere [13]. This may have the potential to impact groundwater quality in situations where potable water supplies overlie sites of deep CO_2 storage.

It is also important to consider the impact resulting from impurities (such as H_2S, SO_X and NO_X) that may be present in the stored CO_2. These could, if they were co-transported within a leaking CO_2 plume, also alter pH and redox conditions in the subsurface environment with associated degradation of water quality. Little work has been undertaken in this area, although Onstott [14] has reported some preliminary modelling studies.

3. Evaluating the significance of microbial activity for CO_2 storage

As discussed above, it is well recognised that microbial activity in subsurface environments is generally slow because of the limited availability and supply rates of energy sources. Consequently, microbial effects may be small or undetectable in the initial period of storage projects, the duration of which will be determined by site-specific characteristics. Nevertheless, many reactions may then become autocatalytic and are extremely difficult to control

once initiated. This is particularly illustrated in areas affected by acid mine drainage where sulphuric acid, generated from microbially-catalysed pyrite oxidation (see the extensive references in Ehrlich and Anderson [15]) has damaged the environment and usually proves very difficult to remediate once pyrite oxidation has commenced [4]. Other examples where unrecognised, gradually accelerating microbial activity has proved extremely damaging and costly to remediate include corrosion of pipelines and subsurface structures [e.g. 16] and damage to London Underground tunnels [17]. Consequently, it is crucial to evaluate the potential significance of CO_2 on microbial populations in the deep subsurface, so that any possible issues can be effectively addressed before a problem arises that is very difficult and expensive to remediate.

In order to examine the feasibility of microbes utilising CO_2 as an energy source, we can consider the fundamental chemical thermodynamic constraints on this process. Lithotrophic microorganisms utilise the energy of redox reactions for their life processes and hence a key issue is what potential oxidation reactions can be coupled to the reduction of CO_2. In terms of a redox half reaction, the latter could be represented as:

$$CO_{2(aq)} + 8H^+ + 8e^- \Rightarrow CH_{4(aq)} + 2H_2O \quad (1)$$

where the free energy of reaction per electron consumed is:

$$\Delta G_r^{1e} = [\Delta G_r^{ss} + 8RTln(10)pH + RTln(10)(aCH_4/aCO_2)]/8 \quad (2)$$

where ΔG_r^{ss} is the free energy of reaction in standard state conditions and the other terms are corrections for pH and the activities of the dissolved gases.

In many deep environments, sulphide minerals are likely reductants that have been shown to commonly participate in microbial redox reactions. Under more oxidising conditions the S from minerals such as pyrite (FeS_2) can be oxidised completely to S(VI) (as SO_4^{2-}) but, in more reducing environments, a wide range of intermediate S oxidation states may form [e.g. 18]. For each possible oxidation half reaction, a free energy of reaction can be calculated which shows a difference dependency on pH and other environmental variables. For the example of pyrite, extreme cases could be:

$$FeS_2 + 10H_2O \Rightarrow FeOOH + 2SO_4^{2-} + 19H^+ + 15e^- \quad (3)$$

where the free energy of reaction per electron produced is:

$$\Delta G_r^{1e} = [\Delta G_r^{ss} + 19RTln(10)pH + 2RTln(10)log(aSO_4^{2-})]/15 \quad (4)$$

and

$$FeS_2 + 2H_2O \Rightarrow FeOOH + 2S^0 + 3H^+ + 3e^- \quad (5)$$

where the free energy of reaction per electron produced is:

$$\Delta G_r^{1e} = [\Delta G_r^{ss} + 3RTln(10)pH]/3 \quad (6)$$

As pH plays a key role in influencing the most energetically favourable reactions, the ΔG_r^{1e} can be plotted as a function of pH without consideration of the other variables. Some examples of pyrite oxidation reactions which could couple to CO_2 reduction in different pH ranges are given in Figure 1. Figure 1 also shows H_2 oxidation as hydrogen is the most common energy source for methanogenesis [15]. In Figure 2 some examples of half reactions for intermediate S oxidation states are shown which could also be coupled to CO_2 reduction. Figure 3 shows

examples of half reactions for impurities that may be present within a leaking CO_2 plume (H_2S, SO_2, NO_2) which are also coupled to CO_2 reduction.

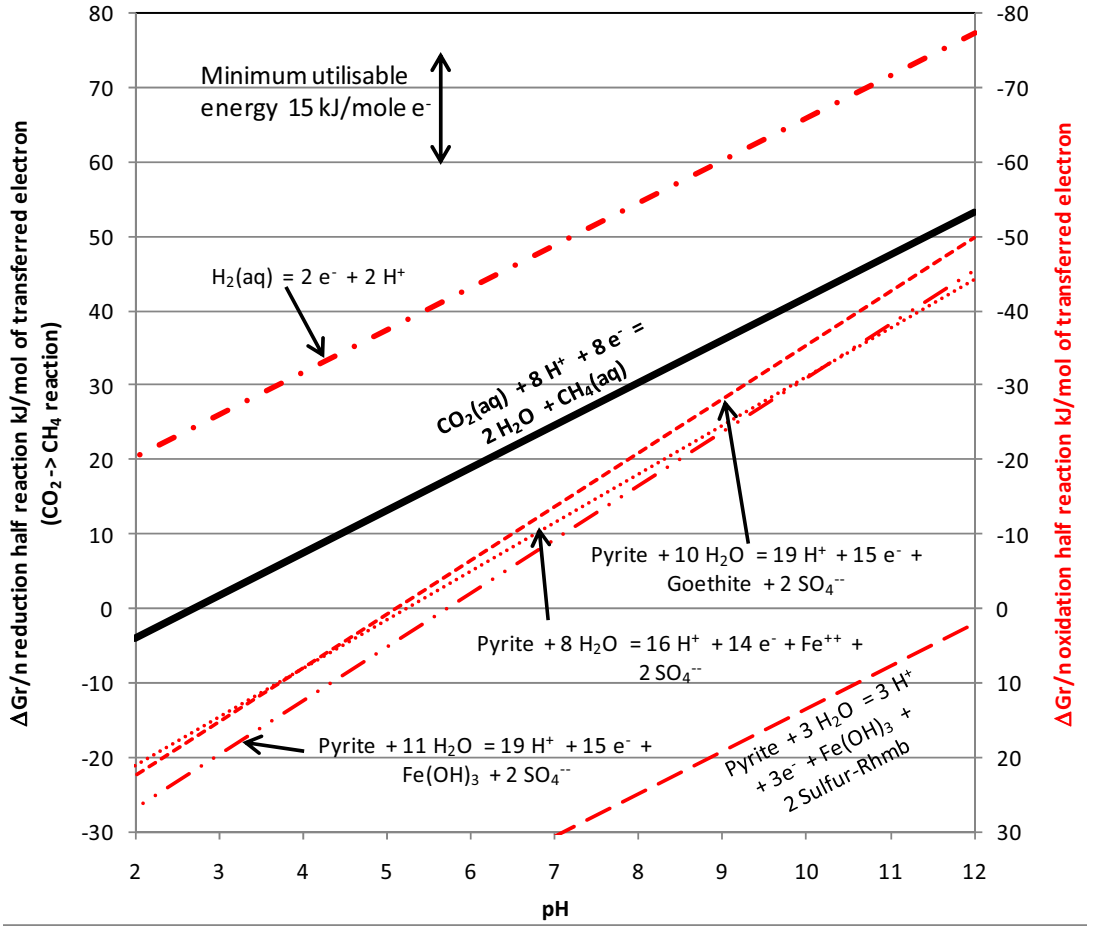

Figure 1. Diagrammatic illustration of the variation of the free energy of some potential pyrite oxidation half-reactions coupled to CO_2 reduction half reaction as a function of pH. CO_2 reduction (solid line) refers to the scale on the left hand side while oxidations (dashed lines) refer to the scale on the right hand scale. For comparison H_2 oxidation is shown as this is a common energy source for methanogenesis. The minimum utilisable energy source for microbial use is also illustrated.

4. Can these reactions generate enough energy for microbial use in a deep geological environment?

The redox half-reaction approach outlined above allows identification of the most exoenergetic oxidation to drive methanogenesis – this being a function of site characteristics (predominantly pH and temperature) and also storage conditions (predominantly the injection pressure of CO_2). There is a limit to the minimum energy that can be practically utilised – generally assumed to be about 15 kJ/mole of electrons transferred [19]. For reactions above this cut-off, the energy available to the microbial populations in a specific region of the reservoir (or its surroundings) is set by availability of the reductant – e.g. quantity of pyrite, its surface area and its degree of contact with fluids. Note that some reactions are net producers or consumers of protons and hence will cause pH drift. If the reaction is more favourable or substrate becomes more available under the new pH, this is autocatalytic and can lead to 'run

away' reactions as discussed above. However, it is clear from Figure 1 that there is not sufficient energy available for microbial methanogenesis from direct pyrite oxidation. Nevertheless, Figure 2 does show that some intermediate S oxidation half reactions above ~pH 4, when coupled to CO_2 reduction, potentially provide enough energy for microbial useage. Observations in other reducing environments suggest that these intermediate oxidation states can form when mineral oxidation is incomplete [18]. Consequently, it is now important to calculate and evaluate the significance of these reactions using information from specific and relevant geological settings.

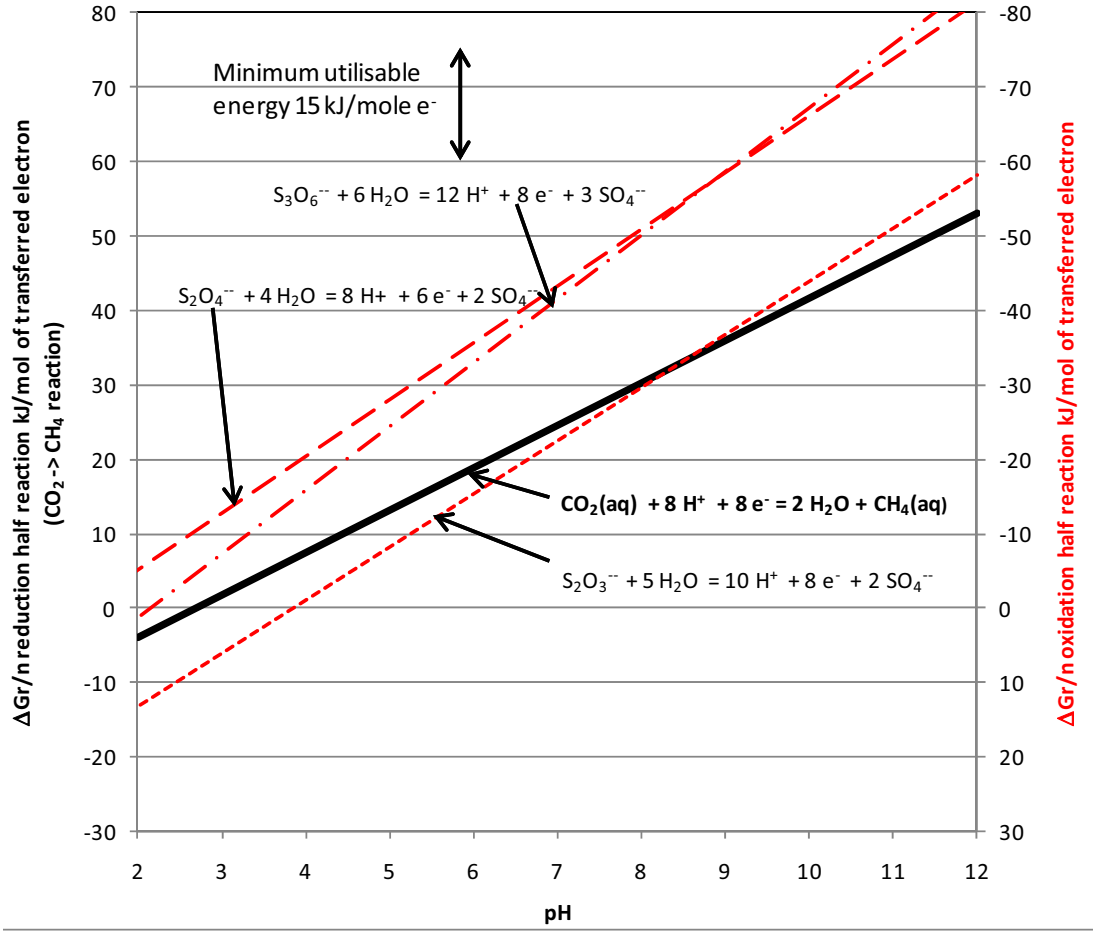

Figure 2. Diagrammatic illustration of the variation of the free energy of some potential intermediate S oxidation half-reactions coupled to CO_2 reduction half reaction as a function of pH. CO_2 reduction (solid line) refers to the scale on the left hand side while oxidations (dashed lines) refer to the scale on the right hand scale. The minimum utilisable energy source for microbial use is also illustrated.

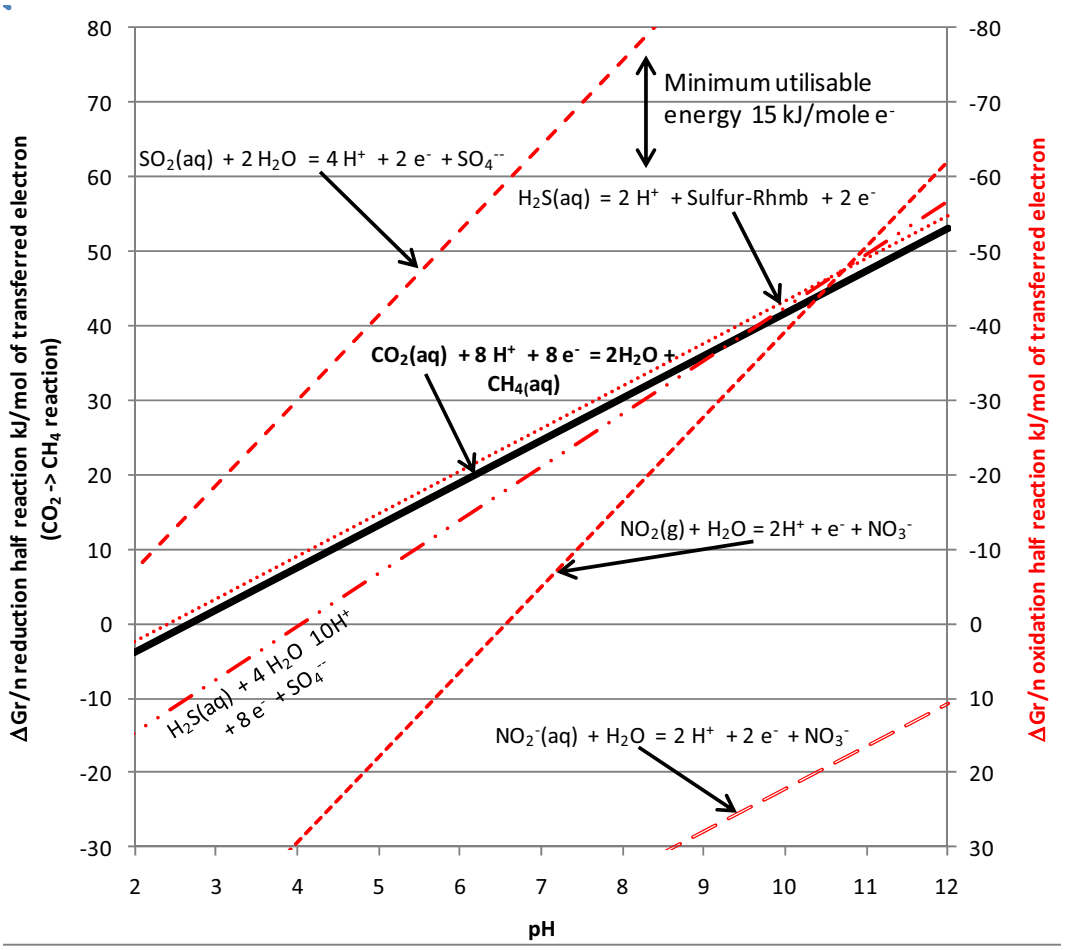

Figure 3. Diagrammatic illustration of the variation of the free energy of some potential impurity half-reactions coupled to CO_2 reduction half reaction as a function of pH. CO_2 reduction (solid line) refers to the scale on the left hand side while oxidations (dashed lines) refer to the scale on the right hand scale. The minimum utilisable energy source for microbial use is also illustrated.

Additionally, Figure 3 shows that SO_2 oxidation can be coupled to CO_2 reduction to provide sufficient energy for microbial useage. This is particularly apparent above ~pH 3 and it should be noted that these coupled reactions will also result in a decrease in pH as well as generating methane. Consequently, the presence of SO_2 as an impurity in injected CO_2 is potentially an area of uncertainty which requires more detailed evaluation. Figure 3 also shows that neither H_2S nor NO_2 half reactions produce sufficient energy for microbial use when coupled to CO_2 reduction.

These calculations can be used in simple models which quantify the impact on a subsurface biological community that can utilise any such energy. One such model is BGSE (Bacterial Growth in Subsurface Environments) [19] jointly developed by the British Geological Survey (BGS) and Nagra (National Cooperative for the Disposal of Radioactive Waste, Switzerland). In this model, microbes are assumed to require 45 kJ/g (dry weight) as maintenance energy and an additional 45 kJ/g (dry weight) for growth. Thus for an active, growing microbial population 90 kJ/g (dry weight) is required. Assuming sufficient nutrients (C, N, P and S) are available in the specific environments so that these do not limit microbial growth, the active, growing population mass of microbes that could be supported for a given amount of reaction can be calculated. This allows the potential consequences of increased biomass, possibly in the forms of biofilms, to be assessed. The main probable influence

of biofilms is likely to be on operational aspects (e.g clogging wells and/or injection equipment). Biofilms also have the potential to seal pore spaces [20].

Such calculations also allow estimation of the potential production rate of methane which could be compared to measurements from injection sites to estimate SO_2 and/or sulphide mineral oxidation rates. If methane were to escape to the atmosphere, it could also act as more powerful greenhouse gas than CO_2. As noted above, the resultant production of H^+ or OH^- can also be calculated, which will either cause a drift of in pH or will be buffered by mineral alteration reactions: in both cases with the potential to release metals present as trace components (e.g in impure sulphides or carbonates). If this release were large enough, it could impact on groundwater quality.

5. What are the possible effects of resulting microbial activity on CO_2 containment – both direct and indirect?

The nature and scale of the geochemical impacts from microbially catalysed redox reactions will be heavily dependent on the characteristics of the geological setting. Although the consequences of slow seepage into aquifers may be of more general concern, in some cases the redox front could develop throughout the cap rock. The extent of the redox front would be controlled by the available nutrients and also the amount of energy available to the microorganism from the utilised redox reactions. The resulting impacts of microbial activity from these reactions could be both physical (e.g. altering porosity through the production of biofilms) and chemical (e.g. changing pH, redox conditions) and may result in intracellular or extracellular mineral formation or degradation [20,21,22,23]. These processes could all directly impact on the physical transport of CO_2 (as a gas or dissolved in fluid) through fractures and porous media. Although it is unlikely that such processes could cause failure of containment, they should, at least, be assessed.

6. Conclusions and future perspectives

The effect of CO_2 on the activity of any indigenous microbial populations and resulting biogeochemical processes is an area of uncertainty, but it is likely that risks may only apply to specific geological settings and/or storage schemes. Given these uncertainties, the precautionary principle suggests that potential impacts should be quantified before projects are initiated. This paper has outlined a microbial energetics approach which can be used to evaluate these risks and it is proposed that a tool is specifically developed to allow rapid and user friendly risk assessment. Suitable background datasets are available for some sites [e.g. 24,25] to allow model development and calibration. However, validation of the modelling approach for timescales in excess of decades/centuries will require data from natural analogue sites.

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